THE RAMAN SPECTRA OF 1, 2- AND 1, 1-DICHLORO-ETHANES IN THE SOLID STATE *

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Plate XII

ABSTRACT. The Raman spectra of 1, 1- dichloroethane and 1, 2- dichloroethane in the solid and liquid states have been studied in order to test the hypothesis put forward by previous authors regarding the co-existence of rotational isomers in the case of 1-2 dichloroethane in the liquid state. It is observed that both the substances yield ten Raman lines having frequency shifts below 1100 cm^{-1} in the liquid state. Some of these lines of 1, 2-dichloroethane disappear when the substance is solidified, but in the case of 1,1-dichloroethane all these lines persist in the solid state. It is pointed out that these results do not support the hypothesis that the extra Raman lines in the liquid state are due to the co-existence of rotational isomers. It is pointed out that the results can be explained on the assumption that strongly associated molecules are present in these two liquids.

INTRODUCTION

The Raman spectra of ethylene dihalides in the solid state were first studied by Mizushima *et al* (1936, 1938). They observed that some important lines disappear in the solid state and explained the phenomenon on the hypothesis that in the solid states the molecules are all in the trans state, while the liquid state contains the molecules of both the trans and gauche or cis configurations. Later, Sirkar and Bishui (1945) studied the Raman spectra of ethylene dibromide in the liquid and the solid state and also the polarisation of the lines due to the liquid state at room temperature, and criticised the hypothesis put forward by Mizushima *et al* showing that the two lines 1056 cm^{-1} and 1441 cm^{-1} of liquid ethylene dibromide were totally depolarised, although according to their hypothesis these lines ought to have been polarised. An alternative hypothesis that in the liquid state some of the molecules might be in a strongly associated state, forming thereby groups having the symmetry C_{2v} and that in the solid state the group might change to one having a symmetry D_{2h} was put forward by Sirkar and Bishui (1945). Further, the results of investigations of the Raman spectra of ethylene dibromide dissolved in different solvents by Bishui and Sanyal (1947), of their polarisation and of the ratio of the intensities of the lines 551 cm^{-1} and 660 cm^{-1} of the pure ethylene dibromide at different temperatures by the present author (1948) seemed to support the view put forward by Sirkar and Bishui (1945). The sure test of the different hypotheses, however, lay in the study of the Raman spectra of dihalogen ethanes in which there can be no rotational

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isomers. By comparing the Raman spectra of such disubstituted ethanes with those of similar molecules which may have rotational isomers one can definitely say whether the presence of rotational isomers is responsible for the presence of too many lines in the Raman spectra of these substances. For this purpose, the Raman spectra of 1, 2-dichloroethane and 1, 1-dichloroethane in the liquid and the solid state have been studied in the present investigation and the results which are described below lead to the definite conclusion that the extra lines present in the Raman spectra of these substances in the liquid state are not due to the presence of rotational isomers.

EXPERIMENTAL

The apparatus used in the present investigation for the study of the Raman spectra of the substances in the solid state at low temperatures was the same as that described earlier by Sirkar and Bishui (1943). Kahlbaum's pure substances distilled in vacuum were put in a double walled cylindrical pyrex glass tube held in a vertical position in the liquid oxygen contained in a transparent Dewar vessel. The interspace between the two walls of the container was evacuated with a Cenco hyvac pump, so that on pouring the liquid oxygen into the Dewar vessel to fill it up to a certain height from the bottom of the container, the temperature of the liquid was lowered very slowly, and consequently the process of solidification also was very slow. The frozen mass thus produced was transparent. The dry air was introduced afterwards into the interspace mentioned above and the temperature of the solid reached a steady value of about—170°C within an hour.

A Fuess glass spectrograph having a dispersion of about 14 A. U. per mm. in the region, 4046A was used. The liquid was illuminated by light from two vertical mercury arcs condensed by two six inch glass condensers placed on the opposite sides of the container. Cobalt-glass filters were placed in the path of the incident light to cut off continuous background in the blue-green region of the spectrum.

The polarisation of the Raman lines was studied qualitatively by photographing the horizontal and vertical components of the scattered light simultaneously on the same plate with the help of a double image prism as usual. The liquid was contained in a horizontal Wood's tube provided with a plane window. Light from a mercury arc focussed with the help of a condenser was used as the incident light in this case also. In the case of totally depolarised lines the horizontal component was more intense than the vertical component in this arrangement.

RESULTS AND DISCUSSION

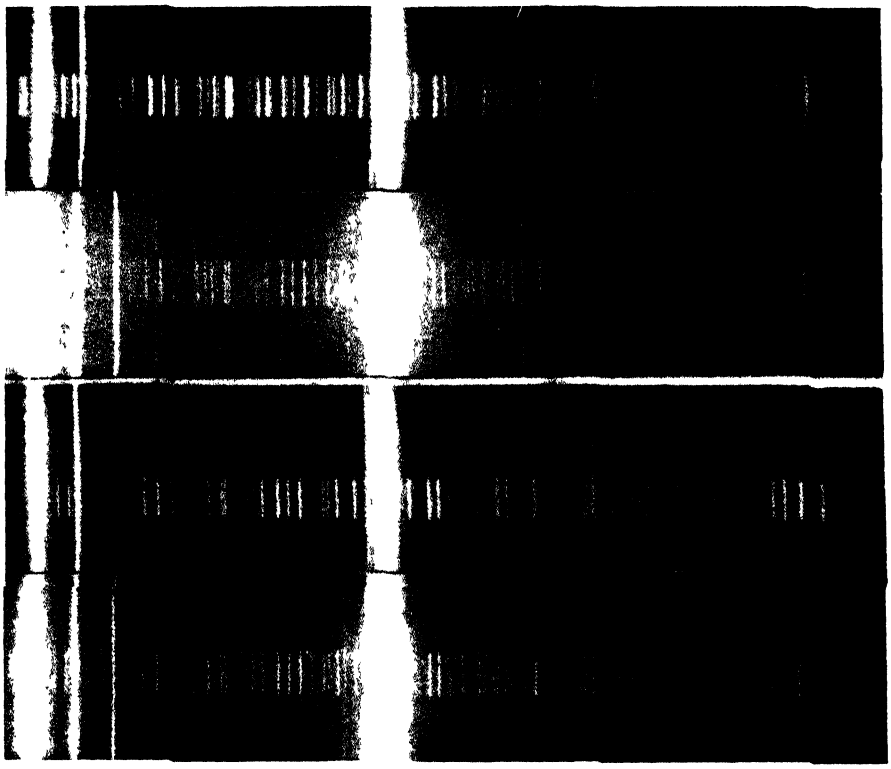
The spectrograms obtained for the liquid and solid states are reproduced in Plate XII.

Fig 1

Fig. 2

Fig 3

Fig 4



Raman Spectra

Fig 1 1, 2 - Dichloroethane at about + 30°C
Fig 2 1, 2 - „ „ „ 170 C
Fig 3 1 1 - Dichloroethane at about + 30°C
Fig 4. 1, 1 - „ „ „ 170°C

The results are given in Tables I and II. The second column of each table contains the results reported by some of the previous workers. The letters P and D denote polarised and totally depolarised ($\rho = 6/7$) respectively. The approximate visually estimated intensities are given in the parentheses. The data for the solid obtained in the present investigation are given in the last column.

TABLE I

1, 2-dichloroethane $ClCH_2.CH_2Cl$.

Liquid State		Solid State	
Present author.	Mizushima *et al* (1938).	Mizushima *et al* (1938) at about—140°C.	Present author at about—170°C.
—	—	53, k ±	58 (2b). k
—	—	74, k ±	82 (1). k
128 (3b)e, k, D	125 (5b)e ±, k ±	V	—
265 (2)e, k; P	265 (5)e ±, k, i	V	264 (2)e, k
301 (6)e, k; P	300 (8)e ±, k, i	303 (5)e, k	300 (2)e, k
409 (2)e, k; D	411 (5)e ±, k, i	V	—
654 (8)e, k; P	654 (8)e ±, k, i, f	V	V
676 (3s)e, k; D	677 (6b)e ±, k; i	V	—
754 (10b)e, k; P	754 (10b)e ±, k, i	748 (10)e, k, i, f, g	749 (8)e, k
833 (1)e, k; D	881 (4)e, k	V	—
—	943 (5)e, k	V	—
943 (3b)e, k, P	989 (2)e, k	—	—
—	1031 (2)e, k	990 (3)e, k	—
1051 (3)e, k, P	1052 (4)e, k	1058 (2)e, k	1057 (1)e, k
1122 (0)e, k; ?	—	—	—
1150 ((2)e, k; D	1145 (3)e, k	—	—
1205 (3)e, k; D	1207 (5)e, k	—	—
1270 (1)e, k; D	1264 (3)e, k	1264 (2)e, k	—
1298 (2)e, k; P	1304 (6)e, k	1298 (3)e, k	1296 (3b)e, k
—	1393 (1)e, k	1312 (1)e, k	—
1426 (3)e, k; D	1429 (6)e, k	1437 (2)e, k	—
1443 (4b)e, k; D	1445 (4b)e, k	1456 (2)e, k	1450 (1b)e, k
2840 (1)e, k; P	2844 (3)e, k	—	—
2877 (2)e, k; P	2874 (4)e, k	2870 (2)k	2880 (1b)e, k
2955 (10)e, k; P	2957 (10)e, k, i	2965 (10)e, k, i, q, p, o	2960 (8)e, k
3004 (6b)e, k; D	3005 (8b)e, k, i	3012 (6)e, k, p	3005 (2)e, k

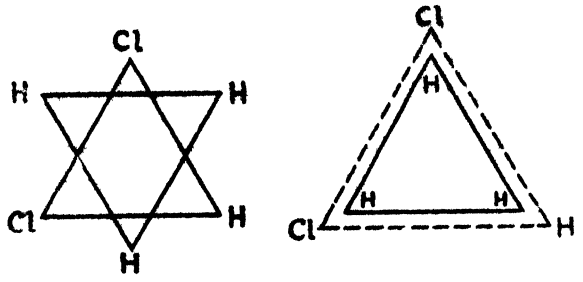
It can be seen from Tables I and II that the number of lines having frequency shifts below 1100 cm^{-1} is ten in the Raman spectra of both 1, 1-dichloroethane and 1, 2- dichloroethane. In the former case almost all the prominent lines persist in the solid state at low temperature and in the latter case some of the prominent lines disappear completely when the substance is solidified. As mentioned earlier this disappearance of the Raman lines of 1, 2- dichloroethane was first observed by Mizushima (1938) and explained on the hypothesis that the molecules having trans and other configurations coexist in the liquid state and the molecules are all of the trans type in the solid state. It was pointed out by Sirkar and Bishui (1945) that this explanation was not satisfactory and an alternative explanation based on the assumption that strongly associated molecules are present in the liquid and

TABLE II

1, 1- dichloroethane $CH_3.CH_2.Cl_2$.

Liquid State		Solid State at about—170°C
Present author.	Magat (1934).	Present author.
—	—	70 (1) k
168 (1b)e, P	—	163 (1b) e, k
275 (4)e±k; P	276 (4)	277 (1) e, k
322 (2)e, k, P	—	322 (1) e, k
408 (3)e, k; P	400 (3)	408 (2) e, k
640 (6)e, k, i, P	642 (6)	640 (3) e, k
688 (3)e, k; D	687 (4d)	680 (2) e, k
905 (0)e, k; ?	978 (2)	977 (1b) e, k
977 (2)e, k, P	—	—
1054 (2)e, k; ?	1050 (0.5d)	1054 (0) e, k
1088 (2b)e, k; ?	1090 (1)	—
1255 (1)e, k, ?	1229 (0)	—
1270 (2)e, k, ?	1271 (1)	—
1352 (2)e, k; D	1353 (0.75d)	—
1442 (5)e, k; D	1438 (2d)	1442 (2) e, k
2930 (6)e, k; P	2929 (6)	2937 (5) e, k
2987 (8b)e, k; D	2985 (5)	2987 (4) e, k
—	—	2996 (3) e, k
3072 (5)e, k; P	3071 (0.25)	3072 (0) e; k

solid states was offered by the latter authors. In the case of 1, 1-dichloroethane on the other hand there is hardly any probability of the existence of two rotational isomers in the liquid state. Of course, we may visualise two different configurations of the molecule, one 'eclipsed' and the other 'staggered', as shown in Fig. 5, but only one such form is stable.



Staggered Eclipsed

Fig. 5

This conclusion is drawn from the experimental results reported by Glockler and Sage (1941) in the case of CCl_3CHFCl. The single configuration of this molecule should yield 18 Raman lines according to group theory and only 18 such lines are also actually observed. From these results and from other evidences Glockler and Sage (1941) have concluded that probably the 'staggered' configuration is stable and the 'eclipsed' one is unstable

in these halogen substituted ethane compounds. Hence in the case of 1, 1-dichloroethane also probably the 'staggered' configuration is the stable one. Since some of the lines are totally depolarised the molecule has a plane of symmetry, but both the forms of the molecule have a plane of symmetry and therefore these data regarding the polarisation of the lines cannot indicate definitely which of the two configurations is actually present in the liquid.

The fact that all the Raman lines having frequency shifts below 1100 cm^{-1} observed in the liquid state are also present in the solid state at about -170° C clearly indicates that only one of two configurations is present in the liquid state. If there were two rotational isomers, the population of one of them would depend on the temperature, and at low temperatures one of the isomers would be converted into the other and consequently the Raman lines yielded by it would disappear at the low temperatures.

Hence the results obtained in the present investigation regarding 1, 1-dichloroethane clearly indicate that the presence of too many lines in the Raman spectrum of this liquid is not due to the presence of rotational isomers

The disappearance of some of the lines of 1, 2-dichloroethane with the solidification of the substance has already been explained by Sirkar and Bishui (1945) on a hypothesis in which it was assumed that associated pairs of molecules having a centre of symmetry are formed in the solid state. The Raman spectrum of 1, 2- dichloroethane in the vapour state has been investigated by Morino, Watanabe and Midzushima (1942). They have come to the conclusion that the gauche molecules are more abundant than trans molecules in the liquid state and the opposite is true in the case of gaseous state. Previously Mizushima *et al* (1938) pointed out that in the solid state all the molecules are in the trans state and that when the substance melts and the molecules have freedom of rotation most of them assume the gauche form. It is, however, difficult to understand how in the gaseous state when such a freedom is greater the number of molecules of gauche form diminishes

In the hypothesis in which the presence of associated molecules is postulated, these facts can be understood easily because in the vapour state most of the molecules become single and the lines due to single molecules become more intense than those due to the associated molecules. In the solid state some of the lines due to the associated molecules disappear because the resultant associated molecule has a centre of symmetry and the oscillations giving rise to these lines are antisymmetric to the centre of symmetry. Of course, from chemical point of view, there may be some difficulty in understanding the nature of the linkage which has been assumed to be responsible for the formation of the associated molecules by Sirkar and Bishui (1945), but the nature of the Raman spectra of the substance at the different states cannot be explained by assuming the co-existence of rotational isomers. There is probably no other alternative than to assume the existence of strongly associated molecules, because the results of present investigation show that

even when no such isomers can be present in the case of 1, 1-dicholoroethane, the number of Raman lines observed is too large for a single molecule.

The appearance of two lines at 58 cm^{-1} and 82 cm^{-1} in the case of 1, 2-dichloroethane and of one line at 70 cm^{-1} in the case of 1, 1- dichloroethane in the solid state is probably due to vibrations of the associated pairs of molecules in which single molecules, oscillate against each other. These lines are differentiated from those due to lattice oscillations because virtual chemical linkages are involved in these modes of vibrations.

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